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FOR MORE INFORMATION
Martine C. Duff, Savannah River National Laboratory
Martine.Duff@srs.gov

Mechanisms of Strontium and Uranium Removal from Radioactive Waste Simulant Solutions by the Sorbent Monosodium Titanate

Martine C. Duff[1], Douglas B. Hunter[1], David T. Hobbs[1], Sam D. Fink[1], Zurong Dai[2], and John P. Bradley[2]

[1]Savannah River National Laboratory; [2]Lawrence Livermore National Laboratory

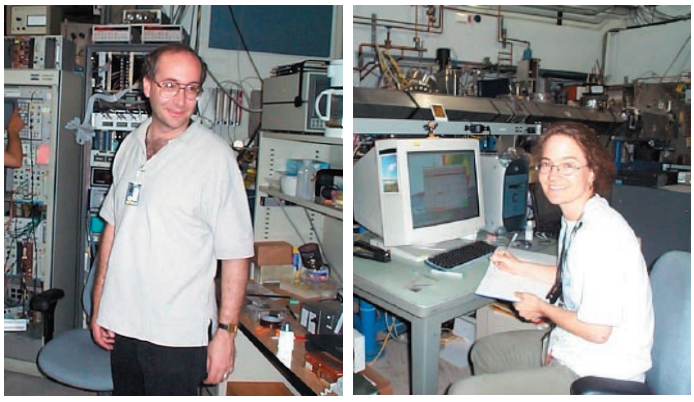
High-Level Radioactive Waste (HLW) is the priority problem for the U.S. Dept. of Energy's Environmental Management Program. Current HLW treatment processes at the Savannah River Site (Aiken, SC) include the use of monosodium titanate (MST, similar to $NaTi_2O_5 \cdot xH_2O$) to concentrate radioactive strontium (Sr) and actinides. Mechanistic information about radionuclide uptake will provide us with insight about the reliability of MST treatments. We characterized the morphology of MST and the chemistry of sorbed Sr^{2+} and uranium [U(VI)] on MST with x-ray based spectroscopic and electron microscopic techniques. Sorbed Sr^{2+} exhibited specific adsorption as partially-hydrated species, whereas sorbed U exhibited site-specific adsorption as monomeric and dimeric U(VI)-carbonate complexes. These differences in site specificity and mechanism may account for the difficulties associated with predicting MST loading and removal kinetics.

High-Level Waste (HLW) is the radioactive waste associated with the dissolution of spent nuclear fuel rods for the recovery of weapons-grade material. At the Savannah River Site (SRS) nearly 130 million liters of HLW await disposal. This waste is highly alkaline and rich in Na^+, NO_3^-, and NO_2^-. Waste treatment involves concentrating the radionuclides (which consists of mainly ^{90}Sr and the actinides, such as U, plutonium, and neptunium) from the waste, and then vitrifying the waste concentrate. Titanate solids, such as monosodium titanate (MST), are chemically stable in high pH solutions, making MST an ideal candidate material for waste treatment.

Our x-ray diffraction studies with MST indicate it is highly amorphous, and scanning electron microscopy reveals that it contains spherical (snowball-like) particles with a typical size range of 5 to 12 μm. Our high-resolution transmission electron microscopy analyses indicate that MST has two prominent morphological populations of titanate material, the first being a very fine fibrous nanocrystalline surficial material, and the second being an amorphous glass-like material (data not shown).

We conducted synchrotron-based x-ray absorption fine structure (XAFS) analyses with Sr- and U-loaded MST that was made by exposing a MST suspension to dissolved Sr and U(VI) (individually) in a HLW simulant solution. Our findings indicate that the sorbed Sr^{2+} and UO_2^{2+} (the uranyl ion) exhibit inner sphere (specific adsorption) sorption behavior with the MST, as opposed to other mechanistic behaviors, such as precipitation, outer sphere adsorption, or structural incorporation with the amorphous MST material (see generalized mechanisms delineated in **Figure 1A-D**).

Our chi XAFS data for the Sr- and U-loaded MST are shown in **Figure 2A and 2B**. The XAFS analyses indicate that the local environment of Sr^{2+} on the MST is partially hydrated (for example, see the spectral comparison with dissolved $SrCl_{2(s)}$ in **Figure 2A**). However, the XAFS data for the outer shells of the added Sr^{2+} indicate that titanium (Ti) atoms are present at two radial distances. We conclude that the Sr^{2+} is sorbed as a partially hydrated species that is specifically adsorbed



Authors Douglas B. Hunter and Martine C. Duff collecting data at the NSLS

on the MST surface—indicating that specific adsorption is the likely Sr uptake mechanism (as described in **Figure 1C**).

Model fits of the U XAFS data indicate that the sorbed U(VI) has an outer shell environment that is consistent with specifically adsorbed U(VI) carbonato species. The data also indicate that at low U(VI) surface loadings, there is specific adsorption of monomeric U(VI) carbonato species at the MST surface (as shown in **Figure 3A**). At high U(VI) surface loadings, however, there is dimerization of sorbed U(VI) carbonato species at the MST surface (as shown in **Figure 3B**).

These studies that characterized the uptake of U and Sr on MST show that there is a strong interaction between MST and the target solution species. This study improves our understanding of this highly amorphous MST material.

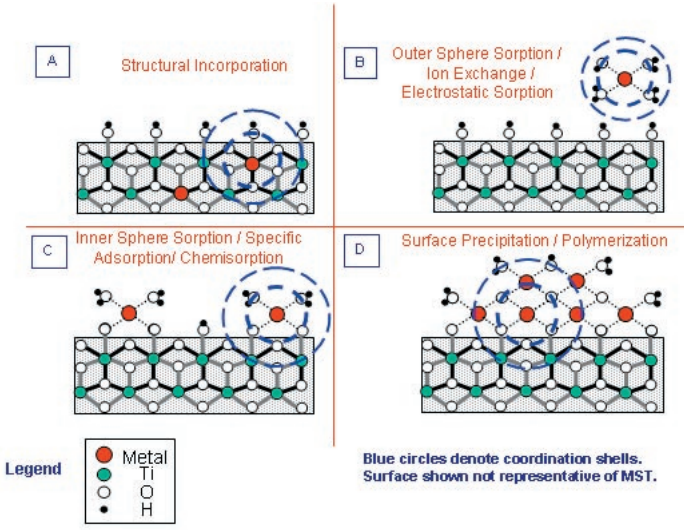


Figure 1. *Mechanisms by which metals can interact with a solids, shown relative to the type of information that can be obtained with XAFS (such as local structural atom identification, radial distances, and coordination number).* **A***) Structural incorporation with MST, where the addition of the metal to the MST-containing solution facilitates precipitation and uptake of metals. In this example, the structural environment appears much like the bulk material that is crystallizing.* **B***) Outer sphere sorption, where the local environment of the sorbed species resembles that of a truly hydrated metal species.* **C***) Inner sphere sorption of the added metal by MST, where a large amount of Ti would be visible in the XAFS data. This is in contrast to outer sphere sorption, where no Ti would exist in the outer shell of the Sr or U XAFS data.* **D***) Precipitation/ polymerization of added metal at or away from the MST surface, where little Ti (from the MST) is observed relative to the outer shell metals that was present in the XAFS data.*

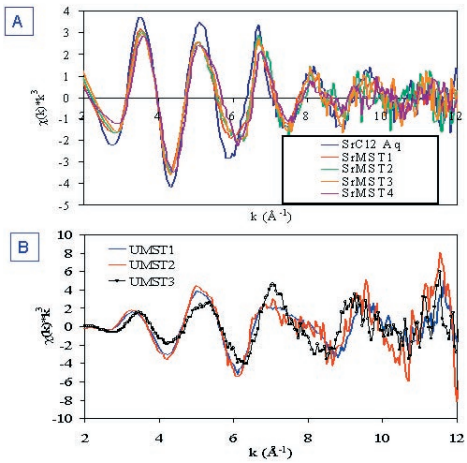


Figure 2. *Chi data for* ***A)*** *Sr (K edge) in the Sr-loaded MST samples and* ***B)*** *for U (L_3 edge) in the U(VI)-loaded MST samples (adapted from Duff et al., 2004).*

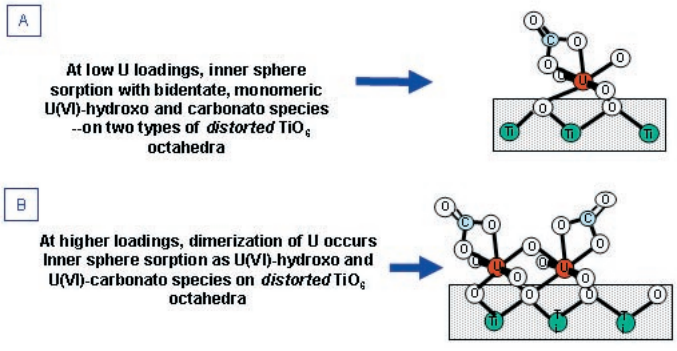


Figure 3. *Atom scale pictorial representations of sorbed U(VI) carbonato species on MST at* ***A)*** *low and* ***B)*** *high U loadings.*